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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Silicone Varnishes

We, TOKYO SHIBAURA ELECTRIC CO., LTD., a corporation duly organized and existing under the laws of Japan, and located at 72 Horikawa-cho, Kawasaki-shi, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to silicone varnishes and more particularly to a silicone varnish which can be dried at comparatively low temperatures.

In order to provide sufficient mechanical and electrical properties to silicon varnishes in addition to their superior heat resistant properties it has normally been necessary to bake the varnishes for long periods at relatively high temperatures (i.e. at 200° to 250°C), in contrast to the baking schedules employed with conventional organic varnishes. This one of the problems encountered when applying silicone varnishes to electric machines and apparatus as an insulating material.

We have now discovered that certain polynuclear complexes are very satisfactory drying catalysts for silicone varnishes without leading to an unacceptably short shelf life for the varnish.

The polynuclear complexes which are employed having the formula $[M_aX_bY_c]Z_d$, M being cobalt or chromium, X is a ligand derived from ammonia, ethylene diamine or water, Y is a bridging group derived from a hydroxo, amido or acetato group, and Z is an acetate group. The subscripts *a*, *b*, *c* and *d* represent the numbers of each atom or group present. The number of transition metals atoms, *a*, may range from 2 to 4.

According to the present invention therefore we provide a silicone varnish which comprises a solution in an organic solvent of an organopolysiloxane resin having the empirical formula:—

$$R_nSiO_{\frac{4-n}{2}}$$

wherein R is a methyl and/or a phenyl group and *n* is from 1.0 to 1.7, and from 0.1 to 3.0% by weight based on said resin, of a polynuclear complex compound of the formula:—

$$[M_aX_bY_c]Z_d$$

wherein M is cobalt or chromium, X is a ligand, derived from ammonia, ethylene diamine or water, Y is a bridging group derived from a hydroxo, amido or acetate group, Z is an acetate group, *a* is the number of transition metals and is an integer from 2 to 4, *b* is the number of ligands, *c* is the number bridging groups and *d* is the number of acetate groups.

The polysiloxanes used as the essential film-forming component are represented by the formula $R_nSiO_{\frac{4-n}{2}}$ where R is a methyl and/or phenyl group (these groups are attached to the silicon atoms) and *n* is the average number of organic radicals attached to each silicon atom; it may range from 1.0 to 1.7. When we speak of R as being a methyl and/or a phenyl group, we mean that the polysiloxanes contain only methyl or phenyl groups directly attached to the silicon atoms, or methyl and phenyl groups so attached. These polymers can suitably be prepared by hydrolysing and polymerising a mixture of chlorosilanes.

The polysiloxanes are dissolved in an organic solvent such as, for example, a mixture of an aromatic hydrocarbon (e.g. benzene, toluene or xylene) and an alcohol (e.g. butanol, diacetone alcohol, isobutyl carbinol or ethylene glycol monoethyl ether).

The polynuclear complex is present in the solution in the range of 0.1 to 3.0% by weight on the resin. As previously stated, its formula is $[M_aX_bY_c]Z_d$ where M is an atom of cobalt or chromium, X is a ligand derived from ammonia, water or ethylene diamine (abbreviated as "en"), Y is a bridging group, that is, a group interconnecting two of the metal atoms, which is derived from a hydroxo group (—OH), an amido group ($—NH_2$) or an acetate group ($CH_3.COO—$), and Z is an acetate group.

Representative polynuclear complex compounds which can be used in the varnishes include: —

$[(NH_3)_4Co(OH)_2Co(NH_3)_4](CH_3COO)_4$,

$[(en)_2Co(OH)_2Co(OH)_2Co(en)_2(H_2O)_2](CH_3COO)_4$,

$[Co\{(OH)_2Co(en)_2\}_3](CH_3COO)_6$

$[Cr\{(OH)_2Cr(en)_2\}_3](CH_3COO)_6$

$[(en)_2Co(OH)_2Co(en)_2](CH_3COO)_4$

$[(NH_3)_4Cr(OH)_2Cr(NH_3)_4](CH_3COO)_4$

$[(NH_3)_4Co(NH_2)(OH)Co(NH_3)_4](CH_3COO)_4$

$[(NH_3)_3Co(OH)_2(CH_3COO)Co(NH_3)_3](CH_3COO)_3$.

It will be seen that more than one type of bridging group or ligand may be present in one complex and further, more than one transition metal may also be present. Further, in the second complex above, it will be seen that the number of anionic acetate groups is one less than normally expected, this is because one of the central cobalt atoms is divalent, as explained by Werner in Berichte der Deutschen Chemischen Gesellshaft, 40 Jahrgang, Bd. Iv, pages 4426—4434 (1907).

These polynuclear complexes can be obtained from the reaction between the corresponding chlorides and silver acetate, from the corresponding sulphate and barium acetate or by neutralising the corresponding hydroxide with acetic acid.

In the polynuclear complexes the numbers of metal atoms, ligands, bridging groups and of acetate groups is, of course, interdependent. For the complexes of cobalt and chromium there can, for example, be deduced the following relationship for the numbers of each atom or group present (considering the simplest types of complexes with only one type of ligand and bridging group): —

The coordination number of cobalt and chromium is 6, bridging groups are bidentate and therefore it follows that

$$b = \frac{6a—2c}{p}$$

where p is the number of co-ordinate bonds which the ligand can form, for example p is 1 for H_2O and 2 for ethylene diamine.

The value of c will be found to vary between (a - 1) to 3(a - 1). The value of *d* is given by the algebraic sum of the total number of electro-valences of the central metal atoms and the total of electric charges on the bridging groups and ligands. For example, in the case of the complex ion

$$[(NH_3)_4Co(OH)_2Co(NH_3)_4],$$

the central metal atoms have 2 × (+3) = +6 valences, the ligands have zero electric charges and the bridging groups have one negative charge apiece, therefore

$$\begin{aligned} d &= 2(+3) + 2(-1) \\ &= 4 \end{aligned}$$

and the formula of the complex is

$$[(NH_3)_4Co(OH)_2Co(NH_3)_4](CH_3COO)_4.$$

When the amount of polynuclear complex in the varnish is less than 1% based on the weight of the polysiloxane, the resin needs to be cured at rather high temperatures but conversely, more than 3% of the complex confers no advantages in curing properties but merely increases the cost of the varnish.

Even polysiloxane resins which normally require curing temperatures of from 200° to 250°C can be cured at somewhat lower temperatures (room temperature to 150°C, for example) for shorter periods of time with the polynuclear complexes according to the invention. Accordingly, the varnishes can be cured by simple heating devices such as infra-red ray lamps, thus simplifying the curing process. In addition, it is possible to use the silicon varnish of this invention quite safely in electrical apparatus which may become heated, possibly to temperatures in excess of 200°C. Moreover, the films formed from the varnishes according to the invention have a reduced tendency to become sticky when subjected to elevated temperatures of 200°C, for example, and once they have been cured the polynuclear complex compounds easily decompose at relatively low temperatures thus providing coated films having superior electrical and heat resistant properties. The silicone varnishes of this invention have good curing rates and shelf stability.

The following Examples are given by way of illustration only in order that the invention may be more fully understood.

EXAMPLE 1

A mixed solvent comprising xylene and butanol (1 : 1) was added to three polysiloxane resins having the following compositions

$$\text{(A)}\quad \frac{R}{Si} = 1.70,\ \frac{CH_3}{C_6H_5} = 1.50,$$

$$\text{(B)}\quad \frac{R}{Si} = 1.56,\ \frac{CH_3}{C_6H_5} = 1.37$$

and

$$\text{(C)}\quad \frac{R}{Si} = 1.47,\ \frac{CH_3}{C_6H_5} = 1.27,$$

respectively, (the resins contained only methyl and phenyl organic groups). The resin solutions were diluted to contain 60%, by weight, of resin component in each case. A polynuclear complex compound

$$[(NH_3)_4Co(OH)_2Co(NH_3)_4](CH_3COO)_4$$

prepared by adding an equivalent amount of acetic acid to a polynuclear complex hydroxide which had been synthesised by reacting

$$[(NH_3)_4Co(OH)_2Co(NH_3)_4](So_4)_2$$

and barium hydroxide was added to each of the resin solutions as the drying catalyst to obtain three types of silicone varnishes.

Table 1 below shows test results of drying, heat resistant and electric properties of these three silicone varnishes and a silicone varnish to which no drying catalyst was added, the testing being made according to JIS (Japanese Industrial Standards) C2122.

TABLE 1

Varnish Samples / Items of test		A		B		C	
Amount of drying catalyst added % *1		0	1.0	0	0.5	0	0.5
Drying temperature and time		250° C. over 6 hrs.	200° C. 3 hrs.	200° C. 1 hr.	150° C. 30 min.	150° C. 10 min.	100° C. 20 min.
Curing rate determined by hot tack test *2		250° C. over 6 hrs.	200° C. 4 hrs.	200° C. 3 hrs.	150° C. 1 hr.	150° C. over 6 hrs.	100° C. 1 hr.
Weight loss at 250° C. after 72 hrs. (%)		5.8	5.5	7.2	6.3	8.5	6.5
Heat endurance at 250° C. flex life (hrs.) *3		over 1000 hrs.	over 1000 hrs.	300 hrs.	300 hrs.	50 hrs.	50 hrs.
Electric strength (kv/0.1 mm)	Normal	8.3	8.0	8.2	8.1	7.8	7.5
	after immersion in water for 24 hrs.	7.7	7.7	8.3	7.8	7.5	7.7
Volume resistivity (Ω-cm)	Normal	over 10^{16}	over 10^{16}	over 10^{16}	over 10^{16}	over 10^{16}	over 10^{16}
	after immersion in water for 24 hrs.	»	»	»	»	»	»
Dielectric constant	25° C.	3.2	3.2	3.0	3.1	3.0	3.0
	180° C.	2.7	2.6	2.5	2.1	2.6	2.6
Dielectric loss tangent (%)	25° C.	0.5	0.7	0.3	0.5	0.4	0.6
	180° C.	1.3	2.5	1.0	0.7	0.9	2.1
Shelf stability	Does not gell after standing for 6 months at room temperature						

Remarks:

*1 percentages, by weight, based on the resin component of the varnish

*2 A drying test in which an asbestos paper measuring 0.3 mm × 25.4 mm × 100 mm is placed on a dried test piece and an iron plate (125 g) measuring 25 mm × 25 mm × 25 mm is placed on the asbestos paper and the hot asbestos can freely fall off after being heated at 200° C. for 15 minutes.

*3 Flex life is the time required for a film of varnish to reach a state where it cracks when bent around a 3 mm. diameter mandrel.

As can be seen from this Example, the present invention enables the curing temperature to be reduced by about 50°C and the curing time to be decreased also. The cured films do not become sticky at elevated temperatures (200°) and furthermore, have low weight loss without affecting heat resistance and electrical properties as well as shelf stability.

EXAMPLE 2

0.5%, by weight, based on the resin component of the solution, of a drying catalyst

$$[(en)_2Co(OH)_2Co(OH)_2Co(en)_2(H_2O)_2](CH_3COO)_4,$$

which was synthesised from

$$[(en)_2Co(OH)_2Co(OH)_2Co(en)_2(H_2O)_2]Cl_4$$

and silver acetate was added to the polysiloxane resin solution (B) of Example 1 and tested by the same method of testing as in Example 1, and it was found that the film was cured after 15 minutes at 150°C and had a flex life (3 mm diam. mandrel) of 500 hours at 250°C.

EXAMPLE 3

$[Co\{(OH)_2Co(en)_2\}_3]Cl_6$ was synthesised from cobalt chloride and ethylenediamine and the polynuclear complex chloride was reacted with silver acetate to obtain a drying catalyst $[Co\{(OH)_2Co(en)_2\}_3](CH_3COO)_6$. This drying catalyst was added to polysiloxane resin solution B of Example 1, respectively in an amount of 0.3, 0.5, 1.0 and 2.0% by weight, based on the resin component of the solution. Table 2 below shows the test results of drying temperature and time of various varnishes using the same method of testing as described in Example 1.

TABLE 2

Amount of drying catalyst added %		0.3	0.5	1.0	2.0
drying temperature and drying time	90° C.	5 hrs.	3 hrs.	2 hrs.	1.5 hrs.
	110° C.	2 hrs.	1.5 hrs.	1 hr.	50 min.
	130° C.	1 hr.	40 min.	30 min.	20 min.
	150° C.	40 min.	20 min.	15 min.	10 min.

The flex life of these varnishes was over 500 hours at 250°C (3 mm diam. mandrel) and their dielectric strength and volume resistivity were also excellent.

EXAMPLE 4

$[Cr\{(OH)_2Cr(en)_2\}_3](SO_4)_3$ was synthesised from potassium chrome alum and ethylene diamine and the polynuclear complex sulphate was reacted with barium acetate to obtain a drying catalyst

$$[Cr\{(OH)_2Cr(en)_2\}_3](CH_3COO)_6.$$

In more detail, ethylene diamine hydrate was added to dehydrated potassium chrome alum, thereby causing an exothermic reaction giving off great amount of heat to obtain a gruel-like substance having a dark violet colour. By heating the thus obtained substance it became a dark red mass consisting mainly of a mixture of

$$K_2SO_4,\ [Cr(en)_3]_2(SO_4)_3 \text{ and}$$

$$[Cr\{(OH)_2Cr(en)_2\}_3](SO_4)_3.$$

By subjecting this mixture to treatment with water,

$$K_2SO_4\ [Cr(en)_3]_2(SO_4)_3$$

passed into solution and

$$[Cr\{(OH)_2Cr(en)_2\}_3](SO_4)_3$$

settled out as a red precipitate. This red precipitate was dissolved as a powder in dilute sulfuric acid and the resultant solution was reacted with barium acetate to obtain

$$[Cr\{(OH)_2Cr(en)_2\}_3](CH_3COO)_6.$$

The drying catalyst was then added to polysiloxane resin solution C of Example 1 in an amount of 0.5%, by weight, based on the resin component of the resin solution and the varnish tested by the same method as was used in Example 1. The film dried within 30 minutes at 100°C and a film dried at 100°C for 2 hours did not show any tackiness at 200°C. Weight loss after heating at 250°C for 72 hours was 6.0%, flex life was 50 hours at 250°C (3 mm diam. mandrel) which was found to be equal to that of films containing no drying catalyst. The electrical properties and the shelf stability were also excellent.

EXAMPLE 5

$$[(en)_2Co(OH)_2Co(en)_2](CH_3COO)_4$$

was synthesised from

$$[(en)_2Co(OH)_2Co(en)_2]Cl_4$$

and silver acetate and the polynuclear complex compound was added to the polysiloxane resin solution B of Example 1 in an amount of 1.0%, by weight based on the resin component of the resin solution and tested by the same method as was used in Example 1. The film cured within 10 minutes at 150°C and 30 minutes at 130°C. The flex life was over 300 hours at 250°C. (3 mm diam. mandrel). This varnish did not gell after standing over 3 months at room temperature.

EXAMPLE 6

$$[(NH_3)_4Cr(OH)_2Cr(NH_3)_4](CH_3COO)_4$$

synthesised from

$$[(NH_3)_4Cr(OH)_2Cr(NH_3)_4](So_4)_2$$

and barium acetate, was incorporated to polysiloxane resin solution B of Example 1 in an amount of 0.5%, by weight based on the resin component of the solution and tested by the same method as in Example 1. It was found that the film dried within 20 minutes at 150°C and that the film which was dried at 150°C for one hour did not show any tackiness at 200°C. The electrical and heat resistant properties of the films were excellent.

EXAMPLE 7

$$[(NH_3)_4Co(NH_2)(OH)Co(NH_3)_4](CH_3COO)_4$$

synthesised from

$$[(NH_3)_4Co(NH_2)(OH)Co(NH_3)_4]Cl_4$$

and silver acetate, was added to polysiloxane resin solution B of Example 1 in an amount of 0.5%, by weight based on the resin component of the resin solution and tested by the same method as in Example 1. It was found that the film dried within 10 minutes at 150°C and that the flex life of a film dried at 130°C for 30 minutes was 400 hours at 250°C (3 mm diam. mandrel).

EXAMPLE 8

$$[(NH_3)_3Co(OH)_2(CH_3COO)Co(NH_3)_3](CH_3COO)_3.$$

synthesised from

$$[(NH_3)_3Co(OH)_2(CH_3COO)Co(NH_3)_3]Cl_3$$

and silver acetate, was added to polysiloxane resin solution C of Example 1 in an amount of 0.5%, by weight based on the resin component of the solution and tested by the same method as in Example 1. The film dried within 30 minutes at 100°C and had good electrical property and shelf stability.

WHAT WE CLAIM IS:—

1. A silicone varnish which comprises a solution in an organic solvent of an organopolysiloxane resin having the empirical formula

$$R_nSiO_{\frac{4-n}{2}}$$

wherein R is a methyl and/or a phenyl group and *n* is from 1.0 to 1.7, and from 0.1 to 3.0% by weight based on said resin, of a polynuclear complex compound of the formula

$$[M_aX_bY_c]Z_d$$

wherein M is a cobalt or chromium, X is a ligand derived from ammonia, ethylene diamine or water, Y is a bridging group derived from a hydroxo, amido or acetate group, Z is an acetate group, *a* is the number of transition metals and is an integer from 2 to 4, *b* is the number of ligands, *c* is the number of bridging groups and *d* is the number of acetate groups.

2. A silicone varnish according to claim 1 in which the polynuclear complex has the formula

$$[Cr\{(OH)_2Cr(en)_2\}_3](CH_3COO)_6.$$

3. A silicone varnish according to claim 1 in which the polynuclear complex has the formula

$$[(NH_3)_4Cr(OH)_2Cr(NH_3)_4](CH_3COO)_4.$$

4. A silicone varnish according to claim 1 in which the polynuclear complex has the formula

$$[(NH_3)_4Co(OH)_2Co(NH_3)_4](CH_3COO)_4.$$

5. A silicone varnish according to claim 1 in which the polynuclear complex has the formula

$$[(en)_2Co(OH)_2Co(OH)_2Co(en)_2(H_2O)_2](CH_3COO)_4.$$

6. A silicone varnish according to claim 1 in which the polynuclear complex has the formula

$$[Co\{(OH)_2Co(en)_2\}_3](CH_3COO)_6.$$

7. A silicone varnish according to claim 1 in which the polynuclear complex has the formula

$$[(en)_2Co(OH)_2Co(en)_2](CH_3COO)_4.$$

8. A silicone varnish according to claim 1 in which the polynuclear complex has the formula

$$[(NH_3)_4Co(NH_2)(OH)Co(NH_3)_4](CH_3COO)_4.$$

9. A silicone varnish according to claim 1 in which the polynuclear complex has the formula

$$[(NH_3)_3Co(OH)_2(CH_3COO)Co(NH_3)_3](CH_3COO)_3.$$

10. A silicone varnish according to any of claims 1 to 9 in which the organic solvent is a mixture of an aromatic hydrocarbon and alcohol.

11. A silicone varnish according to claim 9 in which the aromatic hydrocarbon is benzene, toluene or xylene.

12. A silicone varnish according to claim 9 in which the alcohol is butanol, diacetone alcohol, isobutyl carbinol or ethylene glycol monoethyl ether.

13. A silicone varnish according to any of the preceding claims substantially as herein described in any of the examples.

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